

Observation of excitonic Floquet states in a one-dimensional organic Mott insulator using mid-infrared pump near-infrared probe reflection spectroscopy

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When an electric field of light with a frequency of Ω is applied to a solid, Floquet states, consisting of sidebands with an interval of $\hbar\Omega$ around an electronic state, are expected to be formed. However, only a few studies have experimentally detected such sidebands. Here, we apply mid-infrared pump near-infrared reflection probe spectroscopy to a one-dimensional Mott insulator, bis(ethylenedithio)tetrathiafulvalene-difluorotetracyanoquinodimethane (ET-F₂TCNQ), to detect the transient change in reflectivity R , $\Delta R/R$, due to the formation of excitonic Floquet states. Analyses, considering both odd- and even-parity excitons, demonstrate that the $\Delta R/R$ spectrum reflects the formation of the first-order Floquet sidebands of excitons, and its spectral shape strongly depends on the widths of excitonic states. The experimental and analytical approach reported here is effective in demonstrating excitonic Floquet states in various solids.

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I. INTRODUCTION

According to Floquet's theorem, when a periodic potential with frequency Ω is applied to a solid, sidebands at an interval of $\hbar\Omega$ are formed around an electronic state [1–3]. This quasistationary state, called a Floquet state, is expressed as a superposition of wave functions of those sidebands. Floquet engineering attempts to create a new electronic state by generating such Floquet states [4–14].

Floquet states in solids can be generated by applying a strong electric field using a femtosecond laser pulse, which were detected by time-resolved angle-resolved photoemission spectroscopy in weakly interacting two-dimensional electronic systems of topological materials and van der Waals semiconductors [15–19]. In one-dimensional (1D) systems having strong excitonic effects, sidebands are expected to be formed around excitonic doublon-holon bound states under light electric fields. In a 1D Mott insulator (MI) of a chlorine-bridged nickel-chain compound, [Ni(chxn)₂Cl](NO₃)₂ (chxn = cyclohexanediamine), subcycle spectroscopy was conducted using a phase-stable mid-infrared (MIR) pump pulse and an ultrashort visible probe pulse [20]. The intensity changes in the reflected probe light as well as large coherent oscillations, owing to quantum

interferences between the reflected probe light and radiated lights from the sidebands, were observed. Their spectral analyses demonstrated Floquet sideband formations. However, in subcycle spectroscopy, the available photon energy range is limited [21,22]. Therefore, only few observations of excitonic Floquet states have been reported.

Here, we aimed to detect the excitonic Floquet states in a 1D MI using conventional MIR pump near-IR (NIR) probe spectroscopy. The probe pulse was used to detect the transition from the ground state to excitonic Floquet states generated by the MIR pulse [20,23]. The target material was an organic compound, bis(ethylenedithio)tetrathiafulvalene-difluorotetracyanoquinodimethane (ET-F₂TCNQ) [24]. In ET-F₂TCNQ, an electron is transferred from donors of ET to acceptors of F₂TCNQ [Fig. 1(a)]. F₂TCNQ[−] molecules are nearly isolated, whereas ET⁺ molecules are stacked along the *a* axis, forming a half-filled band [Fig. 1(a)]. Because of the large on-site Coulomb repulsion *U* on ET, electrons are localized on each ET, making this compound a 1D MI [25–27]. Our study shows that by an irradiation of an MIR pulse, the transition to a one-photon allowed exciton is suppressed and transitions to Floquet sidebands are increased. The analysis incorporating third-order optical nonlinearity of odd- and even-parity excitons demonstrates that the reflectivity changes originate from the first-order Floquet sideband formation.

II. EXPERIMENTAL DETAILS

A. MIR pump NIR probe reflection spectroscopy

In the pump-probe reflection spectroscopy [Fig. 2(a)], a Ti:sapphire regenerative amplifier (RA) with a photon energy of 1.55 eV, temporal width of ~ 35 fs, and repetition rate of

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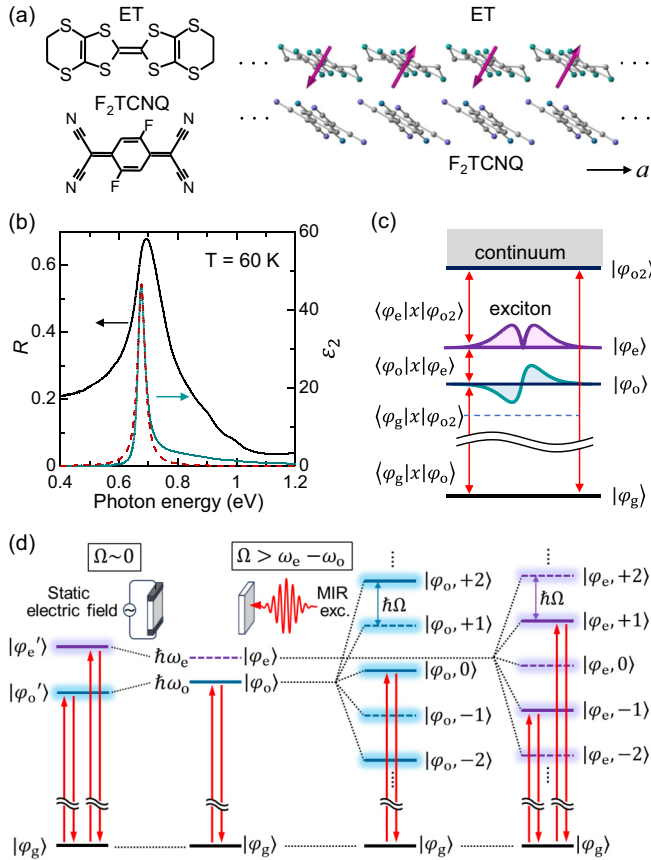


FIG. 1. (a) Molecular and crystal structures of ET-F₂TCNQ. (b) R and ϵ_2 spectra along the a axis. (c) Conceptual excited-state diagram. (d) Conceptual excited-state diagrams under static electric field (left) and MIR electric field with frequency $\hbar\Omega$ (right). Solid and dotted colored lines show one-photon allowed and forbidden states, respectively. Red arrows indicate transitions related to third-order optical nonlinearity.

1 kHz was used. The RA output was divided into two beams. They were input to two optical parametric amplifiers, from which MIR pump pulses (0.15 or 0.25 eV) and NIR probe pulses (0.50–1.1 eV) were generated, respectively. The pump and probe electric fields, E_p and E_r , respectively, were both parallel to ($\parallel$) the a axis. The NIR pulses had temporal widths of ~ 55 fs. The reflected light was introduced into a 10-cm monochromator and detected with a resolution of ~ 10 meV. The measurements were performed at 60 K.

B. Electroreflectance spectroscopy

In the electroreflectance spectroscopy, two electrodes were put on both sides of a single crystal of ET-F₂TCNQ with carbon paste, and an AC electric field with an amplitude of 8.0 kV/cm and frequency of 1 kHz was applied along the a axis. The change in the reflectivity of lights with a polarization parallel to the a axis, $\Delta R/R$, was measured using a lock-in technique. The details of the experimental method were reported previously [28,29]. The measurements were performed at 60 K.

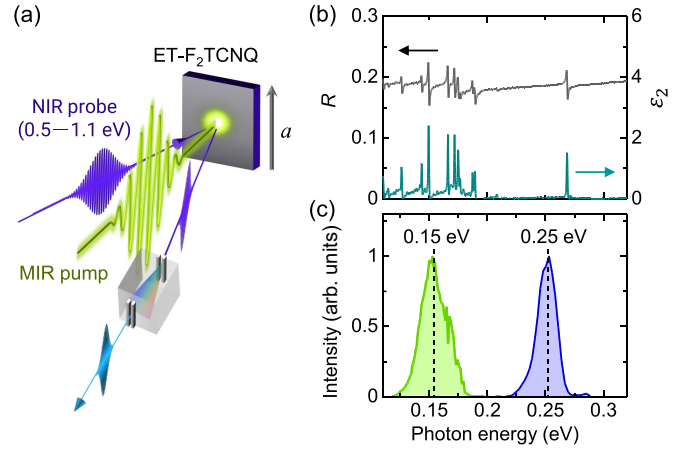


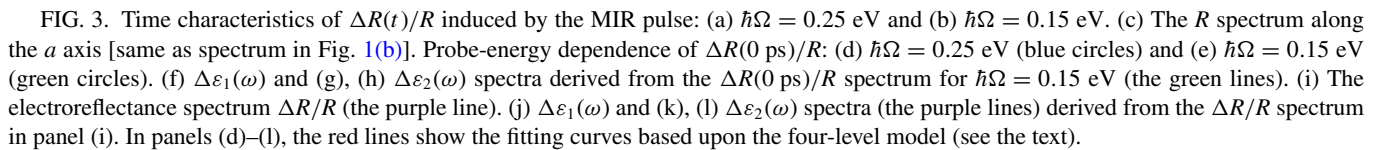
FIG. 2. (a) Schematic of MIR pump NIR probe reflection spectroscopy. (b) R and ϵ_2 spectra along the a axis in ET-F₂TCNQ. (c) Spectra of MIR pump pulses. Each broken line shows the central photon energy of the MIR pulses.

III. RESULTS AND DISCUSSIONS

A. Energy-level structure of excitonic states under a static and MIR electric field

Figure 1(b) shows the $R(\omega)$ and $\epsilon_2(\omega)$ spectra with the light electric field $\parallel a$ in ET-F₂TCNQ. The $\epsilon_2(\omega)$ spectrum was obtained using the Kramers-Kronig transformation (KKT) of the R spectrum. The peak around 0.70 eV is due to the lowest one-photon allowed exciton with odd parity $|\varphi_o\rangle$ [30,31]. Previously, electroreflectance spectroscopy at 294 K using terahertz (THz) pulses showed that the one-photon forbidden exciton with even parity $|\varphi_e\rangle$ was located just above $|\varphi_o\rangle$ and a doublon-holon continuum started at its higher energy side [Fig. 1(c)] [30,31]. Hereafter, the energies of $|\varphi_o\rangle$ and $|\varphi_e\rangle$ are expressed by $\hbar\omega_o$ and $\hbar\omega_e$, respectively.

The predicted energy-level structure of excitonic states under a static and MIR electric field is shown in Fig. 1(d) [20,28]. In 1D MIs, exciton wave functions of $|\varphi_o\rangle$ and $|\varphi_e\rangle$ have similar shapes except for their phases [Fig. 1(c)], and thus, the transition dipole moment between them, $\langle\varphi_o|x|\varphi_e\rangle$, becomes enhanced [28]. This causes large third-order optical nonlinearity [28,29,32–35]; a static electric field strongly hybridizes $|\varphi_o\rangle$ and $|\varphi_e\rangle$, converting them to $|\varphi_o'\rangle$ and $|\varphi_e'\rangle$, respectively. The transition from the ground state $|\varphi_g\rangle$ to $|\varphi_o'\rangle$ shows a redshift and intensity decrease, and the $|\varphi_g\rangle \rightarrow |\varphi_e'\rangle$ transition gains intensity [the red arrows in Fig. 1(d) (the left panel)] [28]. On the other hand, an MIR electric field with a frequency Ω generates sidebands of $|\varphi_o\rangle$ and $|\varphi_e\rangle$, represented by $|\varphi_o, \pm n\rangle$ and $|\varphi_e, \pm n\rangle$ (n : positive integer) [Fig. 1(d) (the right panel)]. $|\varphi_o, 0\rangle$ and $|\varphi_e, 0\rangle$ correspond to the original $|\varphi_o\rangle$ and $|\varphi_e\rangle$ states, showing slight blue- and redshifts, respectively, in the case of $\Omega > \omega_e - \omega_o$ [20]. Optically allowed states are $|\varphi_o, 0\rangle$, $|\varphi_o, \pm 2n\rangle$, and $|\varphi_e, \pm(2n-1)\rangle$. It is expected that the intensity of the $|\varphi_g\rangle \rightarrow |\varphi_o, 0\rangle$ transition reduces as compared with that of the $|\varphi_g\rangle \rightarrow |\varphi_o\rangle$ transition, whereas the $|\varphi_g\rangle \rightarrow |\varphi_o, \pm 2n\rangle$ and $|\varphi_e, \pm(2n-1)\rangle$ transitions gain intensities. Assuming that $\hbar\omega_o \sim \hbar\omega_e$, the condition under which these sidebands can be discriminated is expressed as $\hbar\Omega \gg (\hbar\gamma_o + \hbar\gamma_e)$, using the widths of $|\varphi_o\rangle$, $\hbar\gamma_o$ and $|\varphi_e\rangle$, $\hbar\gamma_e$. For ET-F₂TCNQ,



evaluations of E_{MIR} and τ_{r} are reported in Appendix A. The dependence of $\Delta R(t)/R$ at $t = 0$ ps ($\Delta R(0)/R$) probed at 0.68 eV on E_{MIR} of the 0.15-eV pulse is shown in Fig. 4. $\Delta R(0 \text{ ps})/R$ is proportional to $(E_{\text{MIR}})^2$ up to $E_{\text{MIR}} \sim 1.0$ MV/cm, indicating that the responses for $E_{\text{MIR}} < 1.0$ MV/cm are due to third-order optical nonlinearity; the higher-order responses hardly appear.

The spectra of the MIR pulses are presented in Fig. 2(b) together with the steady-state spectra of reflectivity $R(\omega)$ and imaginary part $[\varepsilon_2(\omega)]$ of complex dielectric constant $\tilde{\varepsilon}(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ in the MIR region. Sharp structures observed in the $R(\omega)$ and $\varepsilon_2(\omega)$ spectra in Fig. 2(b) are the absorptions due to intramolecular vibrations. Since those absorptions are very weak, ET-F₂TCNQ can be considered transparent to the pump lights.

Figure 3 is a plot showing the normalized change in reflectivity, $-\Delta R(0 \text{ ps})/R$, as a function of the electric field, E_{MIR} (in MV/cm). The data points, represented by green triangles, show a linear increase in reflectivity change with increasing electric field, starting from zero at approximately 0.2 MV/cm. A dashed red line indicates a linear fit to the data, and a dashed black line is shown at zero reflectivity change. The text "0.15 eV pump" is present in the upper left corner of the plot area.

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Here, the observed responses are compared with the previous studies of THz and MIR pump-optical reflectivity probe spectroscopy on ET-F₂TCNQ [36,37]. The THz-pump experiment [37] revealed that when the THz electric-field amplitude E_{THz} exceeds 2 MV/cm, carriers are generated via quantum tunneling processes, and the carrier-generation efficiency exhibited a threshold behavior against E_{THz} . Considering the low electric-field amplitude, $E_{\text{MIR}} \sim 0.45$ and 0.66 MV/cm used in Figs. 3(a) and 3(b), respectively, and the relation $\Delta R(0)/R \propto (E_{\text{MIR}})^2$ in Fig. 4, the carrier generation is not the origin of the observed responses. In the previous MIR pump experiment [36], the 0.12-eV pulse with $E_p \perp a$ excited an intramolecular vibration of ET, which modulated the electronic state via the modulation of U . The maximum of $|\Delta R(0)/R|$ around 0.7 eV ($\sim 4\%$) was much smaller than the value ($\sim 13\%$) caused by the 0.15-eV pulse with $E_p // a$ [Fig. 3(e)], although $E_{\text{MIR}} (\sim 2.2$ MV/cm) used in the study [38] was more than 3 times larger than $E_{\text{MIR}} (\sim 0.66$ MV/cm) used here. Other experiments on a dimerized 1D MI revealed that intramolecular a_g -mode vibrations became IR-active due to electron-intramolecular vibration couplings, and their excitations by an MIR pulse modulated the spin states, resulting in the dimerization reduction [39,40]. However, in ET-F₂TCNQ, no dimerizations occur and no strong phonon absorptions exist [Fig. 2(b)]. Thus, we can consider that no structural changes occurred in our case.

The probe-energy dependences of $\Delta R(0)/R$ for the 0.25- and 0.15-eV excitations are shown in Figs. 3(d) and 3(e), respectively, together with the R spectrum [Fig. 3(c)]. In the case that $\hbar\omega_e$ is ~ 50 meV higher than $\hbar\omega_o$, i.e., $\hbar\omega_e \sim 0.73$ eV, as revealed later, the $|\varphi_g\rangle \rightarrow |\varphi_e, \pm 1\rangle$ transitions are expected to appear at $0.73 \text{ eV} \pm \hbar\Omega$, which are indicated by the vertical bars in Figs. 3(d) and 3(e). The $\Delta R(0)/R$ spectrum covers $0.73 \text{ eV} \pm \hbar\Omega$ for $\hbar\Omega = 0.15$ eV but does not cover for $\hbar\Omega = 0.25$ eV. Hence, we analyzed the $\Delta R(0)/R$ spectrum for $\hbar\Omega = 0.15$ eV. The changes in $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$, $\Delta\varepsilon_1(\omega)$ and $\Delta\varepsilon_2(\omega)$, were obtained by KKT of $[R + \Delta R(0 \text{ ps})]$, as shown by the green lines in Figs. 3(f) and 3(g), respectively. The expanded $\Delta\varepsilon_2(\omega)$ spectrum was shown by the green line in Fig. 3(h).

$\Delta\varepsilon_2(\omega)$ represents positive, negative, and positive changes from the low-energy side. In Fig. 3(g), $\hbar\omega_o = 0.676$ eV and predicted energies of $|\varphi_e, \pm 1\rangle$, $\hbar\omega_e + 0.15 \text{ eV} = 0.88 \text{ eV}$ and $\hbar\omega_e - 0.15 \text{ eV} = 0.58 \text{ eV}$, are indicated by green and blue arrows, respectively. The large negative dip and positive change around $\hbar\omega_o$ in $\Delta\varepsilon_2(\omega)$ can be ascribed to the blueshift and intensity decrease of the original $|\varphi_g\rangle \rightarrow |\varphi_o\rangle$ transition, while the absorption increase around 0.6 eV is so broad and that around 0.9 eV does not show a peak structure.

To clarify whether these changes are consistent with the Floquet picture, $\Delta\varepsilon_{1,2}(\omega)$ spectra were simulated. First, the original $\varepsilon_2(\omega)$ spectrum was fitted by a Lorentz oscillator:

$$\varepsilon_2(\omega) = \frac{Ne^2}{\varepsilon_0\hbar} \langle \varphi_g | x | \varphi_o \rangle^2 \text{Im} \left(\frac{1}{\omega_o - \omega - i\gamma_o} + \frac{1}{\omega_o + \omega + i\gamma_o} \right). \quad (1)$$

$\hbar\gamma_o$ is the width of $|\varphi_o\rangle$ and $\langle \varphi_g | x | \varphi_o \rangle$ is the transition dipole moment between $|\varphi_g\rangle$ and $|\varphi_o\rangle$. The fitting curve [the red

TABLE I. Fitting parameters of $\varepsilon_2(\omega)$ in Eq. (1) and $\Delta\varepsilon_2(\omega)$ in the four-level model. The parameters for the fittings of $\varepsilon_2(\omega)$ and $\Delta\varepsilon_2(\omega)$ are accurate to three and two significant digits, respectively.

$\hbar\omega_o$ (eV)	$\hbar\gamma_o$ (eV)	$\hbar\omega_e$ (eV)	$\hbar\gamma_e$ (eV)	$\hbar\omega_{o2}$ (eV)	$\hbar\gamma_{o2}$ (eV)
0.676	0.0152	0.73	0.050	0.78	0.080
$\langle \varphi_g x \varphi_{o1} \rangle$ (Å)		$\langle \varphi_o x \varphi_e \rangle$ (Å)		$\langle \varphi_g x \varphi_{o2} \rangle \langle \varphi_{o2} x \varphi_e \rangle$ (Å ²)	
1.52		9.8		-6.25	

broken line in Fig. 1(b)] with the parameters in Table I reproduced the experimental result.

Then, we analyzed the $\Delta\varepsilon_1(\omega)$ and $\Delta\varepsilon_2(\omega)$ spectra using $\chi^{(3)}(-\omega; \Omega, -\Omega, \omega)$ based on the three-level model, in which $|\varphi_g\rangle$, $|\varphi_o\rangle$, and $|\varphi_e\rangle$ are considered [30,41]. The general expression of $\chi^{(3)}$ for this model is given by Eq. (B5) in Appendix B. In the framework of third-order optical nonlinearity, the following relationship stands between $\Delta\tilde{\varepsilon}(\omega)$ and $\chi^{(3)}(-\omega; \Omega, -\Omega, \omega)$ [41]:

$$\Delta\tilde{\varepsilon}(\omega) = \frac{3}{2} \chi^{(3)}(-\omega; \Omega, -\Omega, \omega) E(\Omega) E(-\Omega). \quad (2)$$

As $\hbar\omega_o$, $\hbar\gamma_o$, and $\langle \varphi_g | x | \varphi_o \rangle$ had been determined (Table I), the fitting parameters were the energy $\hbar\omega_e$ and width $\hbar\gamma_e$ of $|\varphi_e\rangle$ and the transition dipole moment $\langle \varphi_o | x | \varphi_e \rangle$ between $|\varphi_o\rangle$ and $|\varphi_e\rangle$. However, the $\Delta\varepsilon_1(\omega)$ and $\Delta\varepsilon_2(\omega)$ spectra could not be reproduced.

Therefore, we next attempted the four-level model, in which another one-photon allowed state with odd parity $|\varphi_{o2}\rangle$ was added on the higher-energy side of $|\varphi_e\rangle$ [30,34,42]. The general expression of $\chi^{(3)}$ for this model and the main term of $\chi^{(3)}(-\omega; \Omega, -\Omega, \omega)$ are given by Eqs. (B6) and (B7), respectively, in Appendix B. The four-level model could explain the $\Delta\varepsilon_2(\omega)$ and $\chi^{(3)}(-\omega; 0, 0, \omega)$ spectra obtained by the THz electroreflectance spectroscopy [30]. In this model, the energy $\hbar\omega_{o2}$ and width $\hbar\gamma_{o2}$ of $|\varphi_{o2}\rangle$ and the product of the transition dipole moments $\langle \varphi_e | x | \varphi_{o2} \rangle \langle \varphi_g | x | \varphi_{o2} \rangle$ are additional parameters.

Using this model, the $\Delta\varepsilon_1(\omega)$, $\Delta\varepsilon_2(\omega)$, and $\Delta R(0)/R$ spectra were well reproduced as shown by the red lines in Figs. 3(e)–3(h) with the parameters listed in Table I. Both the experimental and calculated $\Delta\varepsilon_2(\omega)$ spectra show that the absorption increases occur around 0.60 eV and in the range 0.69–0.88 eV. These results are not coincident with the simple prediction from the Floquet formalism predicting that the absorption increases at $\hbar\omega_e + 0.15 \text{ eV} = 0.88 \text{ eV}$ and $\hbar\omega_e - 0.15 \text{ eV} = 0.58 \text{ eV}$ (blue arrows). A possible reason is that the widths of exciton states cannot be neglected compared to the energy interval between $|\varphi_o\rangle$ and $|\varphi_e, +1\rangle$ or $|\varphi_e, -1\rangle$, which is $(\hbar\omega_e + \hbar\Omega) - \hbar\omega_o \sim 0.20 \text{ eV}$ or $\hbar\omega_o - (\hbar\omega_e - \hbar\Omega) \sim 0.10 \text{ eV}$ for $\hbar\Omega = 0.15 \text{ eV}$. $(\hbar\gamma_o + \hbar\gamma_e) = 0.0652 \text{ eV}$ is not negligibly small compared to those intervals. Since $\hbar\gamma_e (= 0.050 \text{ eV})$ is significantly larger than $\hbar\gamma_o (= 0.0152 \text{ eV})$, therefore, $\hbar\gamma_e$ might influence the spectral shapes of $\Delta\varepsilon_{1,2}(\omega)$.

To clarify this, we calculated the $\hbar\gamma_e$ dependence of $\Delta\varepsilon_2(\omega)$. In this calculation, we adopted the simpler three-level

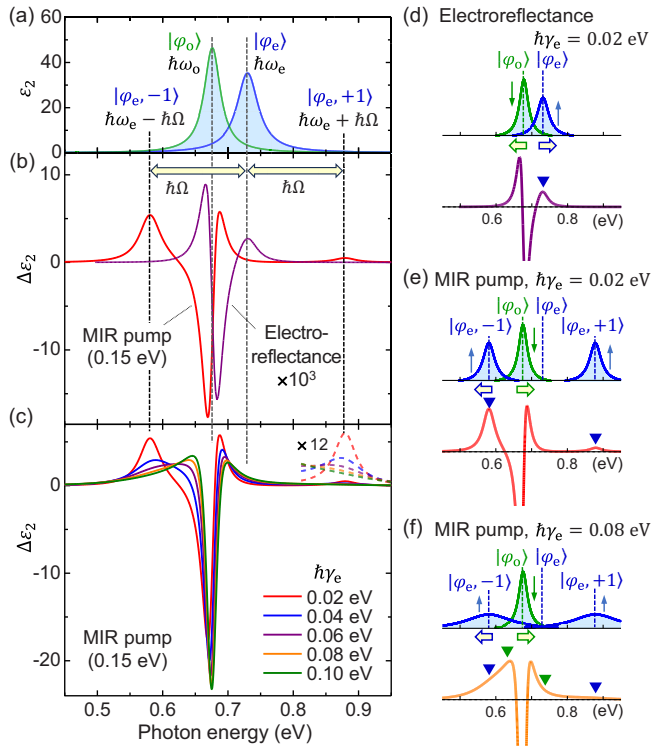


FIG. 5. (a) The simulated ε_2 spectrum of $|\varphi_0\rangle$ and Lorentzian spectrum of $|\varphi_e\rangle$ (arbitrary unit). Simulation of $\Delta\varepsilon_2$ spectra based upon the three-level model: (b) red line: 0.15-eV pump with $\hbar\gamma_2 = 0.02$ eV; purple line: electroreflectance with $\hbar\gamma_2 = 0.02$ eV; and (c) 0.15-eV pump with $\hbar\gamma_2 = 0.02$ – 0.10 eV. Interpretations of $\Delta\varepsilon_2$ spectra: (d) electroreflectance with $\hbar\gamma_2 = 0.02$ eV; (e) 0.15-eV pump with $\hbar\gamma_2 = 0.02$ eV; and (f) 0.15-eV pump with $\hbar\gamma_2 = 0.08$ eV. In the simulations, $\hbar\gamma_1 = 0.0152$ eV was used. Arrows in panels (d)–(f) show schematically the changes of ε_2 .

model to see the broadening effect of $|\varphi_e\rangle$ clearly and used the parameter values of $\hbar\omega_{0,e}$, $\hbar\gamma_{0,e}$, $\langle\varphi_g|x|\varphi_0\rangle$, and $\langle\varphi_0|x|\varphi_e\rangle$ listed in Table I. Figure 5(a) shows the Lorentzian spectra of $|\varphi_{0,e}\rangle$. Figure 5(b) (the red line) shows the $\Delta\varepsilon_2(\omega)$ spectrum for $\hbar\gamma_0 = 0.0152$ eV and $\hbar\gamma_e = 0.020$ eV, the latter of which is much smaller than the actual value $\hbar\gamma_e = 0.050$ eV. Absorption increases at $\hbar\omega_e \pm \hbar\Omega$ predicted for $|\varphi_e, \pm 1\rangle$, which is illustrated in Fig. 5(e). $\Delta\varepsilon_2(\omega)$ near $\hbar\omega_0$ is asymmetric, showing a large negative dip at the lower-energy side and a small positive peak at the high-energy side. This spectral change clearly shows that the $|\varphi_g\rangle \rightarrow |\varphi_0, 0\rangle$ transition reduces and shifts to higher energy [Fig. 5(e)]. As $\hbar\omega_e > \hbar\omega_0$, $|\varphi_e, -1\rangle$ is closer to $|\varphi_0, 0\rangle$ compared with $|\varphi_e, +1\rangle$ as shown in the right part of Fig. 1(d), and $|\varphi_e, -1\rangle$ interacts with $|\varphi_0, 0\rangle$ more strongly than $|\varphi_e, +1\rangle$. This causes the state $|\varphi_0, 0\rangle$ to be pushed to a higher energy than $|\varphi_0\rangle$.

Figure 5(c) shows the $\Delta\varepsilon_2(\omega)$ spectra when $\hbar\gamma_e$ is varied from 0.02 to 0.10 eV with the same values of the other parameters. As $\hbar\gamma_e$ increases, the peaks due to $|\varphi_e, +1\rangle$ and $|\varphi_e, -1\rangle$ become broad. Simultaneously, a positive absorption change appears on the slightly lower-energy side of the absorption decrease at 0.68 eV. This can be explained as follows. Absorptions due to $|\varphi_e, \pm 1\rangle$ should appear at the energies where the density of state of $|\varphi_e, \pm 1\rangle$ is high. If

$\hbar\gamma_e$ is sufficiently smaller than $\hbar\Omega = 0.15$ eV, this factor dominates the induced absorptions and the absorption peak due to $|\varphi_e, -1\rangle$ ($|\varphi_e, +1\rangle$) appears at $\hbar\omega_e - \hbar\Omega$ ($\hbar\omega_e + \hbar\Omega$) as shown by the blue triangles in Fig. 5(e). As $\hbar\gamma_e$ increases, the overlap between $|\varphi_e, -1\rangle$ ($|\varphi_e, +1\rangle$) and $|\varphi_0\rangle$ increases as shown in Fig. 5(f), which strengthens the interaction between them. This enhances the induced absorptions in the region close to $|\varphi_0\rangle$. When this effect becomes dominant, the absorption at $\hbar\omega_e - \hbar\Omega$ ($\hbar\omega_e + \hbar\Omega$) is relatively decreased, but that at the energy somewhat closer to $\hbar\omega_0$ increases. In fact, for $\hbar\gamma_e = 0.08$ eV, new structures appear around 0.64 and 0.74 eV as indicated by the green triangles in Fig. 5(f), leaving weak structures around 0.58 and 0.88 eV (the blue triangles), corresponding to $\hbar\omega_e - \hbar\Omega$ and $\hbar\omega_e + \hbar\Omega$, respectively. In the experiments, the shoulder structures were indeed observed around 0.58 and 0.64 eV as seen in Fig. 3(h), which correspond to the blue and green triangles, respectively, in the low-energy side in Fig. 5(f). On the high-energy side, a peak structure is not clearly observed but the spectral weights appear at the lower energies than $\hbar\omega_e + 0.15$ eV [Fig. 3(h)]. It can be attributed to the fact that the overlap of the states $|\varphi_0, 0\rangle$ and $|\varphi_e, +1\rangle$ occurs only at the lower energies than $\hbar\omega_e + \hbar\Omega$. From these observations, it is clear that the intensity of the $|\varphi_g\rangle \rightarrow |\varphi_0\rangle$ transition decreases and the induced absorptions appear on both sides of the $|\varphi_g\rangle \rightarrow |\varphi_0\rangle$ transition, regardless of $\hbar\gamma_e$ values. These results identified the excitonic sideband states $|\varphi_e, +1\rangle$, $|\varphi_0, 0\rangle$, and $|\varphi_e, -1\rangle$ and demonstrated that the excitonic Floquet states are formed under the MIR electric fields.

For the 0.25-eV excitation, $\Delta\varepsilon(\omega)$ could not be deduced because of the lack of low-energy $\Delta R/R$ data. Therefore, we calculated $\Delta R(0)/R$ by the four-level model using the parameter values in Table I. The obtained spectrum multiplied by 4.2 nearly reproduced the $\Delta R(0)/R$ spectrum as shown by the red line in Fig. 3(d). The difference in magnitude of the experimental and calculated spectra might be attributed to an error in the estimation of E_{MIR} .

C. Spectral changes under a static electric field and their analyses

Considering the changes of the excitonic states shown in Fig. 1(d), a significant difference is expected to appear between the spectral changes by the MIR electric field and those by the static or THz electric field. The previous THz-pump NIR-probe reflection spectroscopy revealed that the $\Delta R/R$ spectrum under the THz electric field at 294 K [30] shows positive, negative, and positive signals with increase of energy, which can be interpreted with the excitonic-state changes shown in the left part of Fig. 1(d). Those spectral changes should be compared with the spectral changes of $\Delta R/R$ under the 0.15-eV excitation at 60 K shown in Fig. 3(e). However, the measured temperatures are different in those two experiments. Therefore, it is difficult to compare their spectral shapes precisely. Considering this, we performed the electroreflectance spectroscopy on ET-F₂TCNQ at 60 K at which the MIR-pump NIR-probe reflection spectroscopy was performed. The obtained $\Delta R/R$ spectrum is shown by the purple line in Fig. 3(i). By applying KKT to this spectrum, we calculated the $\Delta\varepsilon_1(\omega)$ and $\Delta\varepsilon_2(\omega)$ spectra, which are shown

by the purple lines in Figs. 3(j) and 3(k), respectively. In Fig. 3(l), the $\Delta\epsilon_2(\omega)$ spectrum is expanded to see clearly the spectral shape (the purple line).

In the electroreflectance spectroscopy, $\Delta\tilde{\epsilon}(\omega)$ is related to the third-order nonlinear susceptibility $\chi^{(3)}(-\omega; 0, 0, \omega)$ by the following formula:

$$\Delta\tilde{\epsilon}(\omega) = 3\chi^{(3)}(-\omega; 0, 0, \omega)E(0)E(0). \quad (3)$$

Here, $E(0)$ is the applied electric field. In Figs. 3(j) and 3(k), the right vertical axis is $\text{Re}\chi^{(3)}(-\omega; 0, 0, \omega)$ and $\text{Im}\chi^{(3)}(-\omega; 0, 0, \omega)$, respectively. These $\text{Re}\chi^{(3)}(-\omega; 0, 0, \omega)$ and $\text{Im}\chi^{(3)}(-\omega; 0, 0, \omega)$ spectra were simulated using the same four-level model as that used for the analyses of the $\text{Re}\chi^{(3)}(-\omega; \Omega, -\Omega, \omega)$ and $\text{Im}\chi^{(3)}(-\omega; \Omega, -\Omega, \omega)$ spectra obtained by the MIR pump NIR reflectivity probe spectroscopy (Appendix C). The simulated spectra were shown by the red lines in Figs. 3(j)–3(l), which reproduced well the experimental $\Delta R/R$, $\text{Re}\chi^{(3)}(-\omega; 0, 0, \omega)$ ($\Delta\epsilon_1$) and $\text{Im}\chi^{(3)}(-\omega; 0, 0, \omega)$ ($\Delta\epsilon_2$) spectra. In this simulation, $\hbar\gamma_1$ was slightly changed from the value (0.0152 eV) in Table I to 0.018 eV, while the other parameters were fixed to the values in Table I used in the analyses of the $\text{Re}\chi^{(3)}(-\omega; \Omega, -\Omega, \omega)$ ($\Delta\epsilon_1$) and $\text{Im}\chi^{(3)}(-\omega; \Omega, -\Omega, \omega)$ ($\Delta\epsilon_2$) spectra. The success of the simulations of the $\Delta R/R$, $\Delta\epsilon_1$, and $\Delta\epsilon_2$ spectra under both the MIR electric fields and static electric field using almost the same parameters demonstrated the validity of our analyses.

D. Comparison of spectral changes under static and MIR electric field

Now we can discuss the differences in the spectral shapes of $\Delta R/R$, $\Delta\epsilon_1$, and $\Delta\epsilon_2$ under the MIR and static electric fields. In the $\Delta R/R$ spectra, a sequence of positive, negative, and positive signals is observed in the 0.25-eV excitation, 0.15-eV excitation, and static electric field, respectively, in common. However, the energy ranges where each spectral change was observed are different between three cases. The $\Delta\epsilon_{1,2}$ spectra under the 0.15-eV excitation and static electric field are also significantly different. Especially, from the difference of the $\Delta\epsilon_2$ spectra under the 0.15-eV excitation and static electric field shown in Figs. 3(h) and 3(l), respectively, we can deduce how the spectral changes experimentally obtained depend on the frequency of external fields.

The $\Delta\epsilon_2$ spectrum under the static electric field in Fig. 3(l) shows a sequence of positive, negative, positive, and negative signals. Around the original peak due to the $|\varphi_g\rangle \rightarrow |\varphi_o\rangle$ transition at $\hbar\omega_o$, positive and negative signals appear with increase of energy. These signals reveal the low-energy shift of this transition. Another positive signal is observed around the one-photon forbidden exciton $|\varphi_e\rangle$ at $\hbar\omega_e$ in the high-energy side. Those signals can be explained by the electric field-induced mixing of $|\varphi_o\rangle$ and $|\varphi_e\rangle$ and converting $|\varphi_o\rangle$ to $|\varphi_o'\rangle$ and $|\varphi_e\rangle$ to $|\varphi_e'\rangle$ [the left part of Fig. 1(d)]. This mixing gives rise to the low-energy shift of $|\varphi_o\rangle$ and high-energy shift of $|\varphi_e\rangle$. Simultaneously, the $|\varphi_g\rangle \rightarrow |\varphi_o'\rangle$ transition decreases its intensity relative to the original $|\varphi_g\rangle \rightarrow |\varphi_o\rangle$ transition and the $|\varphi_g\rangle \rightarrow |\varphi_e'\rangle$ transition becomes optically allowed gaining the intensity. These are the reasons why the negative signal is larger than the positive signal around $\hbar\omega_o$ and

another positive signal appears at $\hbar\omega_e$ in the $\Delta\epsilon_2$ spectrum of Fig. 3(l). The small negative signal observed around 0.79 eV is attributable to the presence of another optically allowed state $|\varphi_{o2}\rangle$, which is assumed to locate at $\hbar\omega_{o2} = 0.78$ eV in the four-level model. Since $|\varphi_e\rangle$ is also mixed with $|\varphi_{o2}\rangle$, the resultant $|\varphi_g\rangle \rightarrow |\varphi_{o2}'\rangle$ transition is considered to lose its intensity. This is the reason why $\Delta\epsilon_2$ becomes negative around 0.79 eV. This small negative structure was also almost reproduced by the simulation as shown by the red broken line in Fig. 3(l).

The $\Delta\epsilon_2$ spectrum in Fig. 3(h) obtained by the MIR (0.15 eV) excitation also shows a sequence of positive, negative, and positive signals as mentioned above. Around the original peak due to the $|\varphi_g\rangle \rightarrow |\varphi_o\rangle$ transition at $\hbar\omega_o$, however, negative and positive signals appear with increase of energy, which is contrast to the positive and negative signals in the $\Delta\epsilon_2$ spectrum under the static electric field in Fig. 3(l) obtained by the electroreflectance spectroscopy. As discussed in Sec. III B, this indicates that the $|\varphi_g\rangle \rightarrow |\varphi_o, 0\rangle$ transition shows a high-energy shift relative to the original peak due to the $|\varphi_g\rangle \rightarrow |\varphi_o\rangle$ transition at $\hbar\omega_o$. Such a blueshift is characteristic of the condition $\Omega > \omega_e - \omega_o$ [20]. The positive signals in the range from 0.55 to 0.65 eV and from 0.73 to 0.88 eV can be attributed to the presence of the Floquet sideband states of $|\varphi_e, -1\rangle$ (the $|\varphi_g\rangle \rightarrow |\varphi_e, -1\rangle$ transition) and $|\varphi_e, +1\rangle$, respectively. A small negative signal around 0.9 eV might be due to the presence of another one-photon allowed state $|\varphi_{o2}\rangle$ at $\hbar\omega_{o2} = 0.78$ eV as discussed in the previous section. The simulation curve obtained using the four-level model considering $|\varphi_{o2}\rangle$ [the red solid and broken lines in Fig. 3(h)] well reproduced the experimental $\Delta\epsilon_2$ spectrum in the wide energy region. It demonstrates that our interpretation based upon the Floquet picture, that is, the formation of the Floquet sideband states, is valid.

These differences in the $\Delta\epsilon_2$ spectra under the static and MIR electric fields should be seen much more clearly in the case that the widths of excitonic states are small. In Fig. 5(b), the $\Delta\epsilon_2(\omega)$ spectrum under a static electric field calculated using the simple three-level model with $\hbar\gamma_o = 0.0152$ eV and $\hbar\gamma_e = 0.020$ eV was shown by the purple line, together with the $\Delta\epsilon_2(\omega)$ spectrum under the MIR (0.15 eV) electric field calculated using the same model with the same parameter set (the red line). The spectral shape of $\Delta\epsilon_2$ under the static electric field (the purple line) is entirely different from that under the MIR electric field (the red line). Such a difference should be observed more clearly in the 1D MIs where the widths of excitonic states are sufficiently small. The analysis of the temperature dependence of $\epsilon_2(\omega)$ spectra previously reported revealed that the width of the lowest excitonic state in 1D MIs is mainly dominated by the electron-lattice interaction [29]. In the 1D MIs with small electron-lattice interaction such as a bromine-bridged nickel-chain compound $[\text{Ni}(\text{chxn})_2\text{Br}]\text{Br}_2$, where $\hbar\gamma_o$ and $\hbar\gamma_e$ are 7 and 38 meV, respectively, at 77 K [29], it will be possible to identify the Floquet sidebands more easily.

Finally, let us overview the systematic changes of $\Delta R/R$, $\Delta\epsilon_1$, and $\Delta\epsilon_2$ induced by the 0.25- and 0.15-eV excitations and static electric field. In Fig. 6, we show their simulated spectra obtained using the four-level model with the parameters in Table I together. Those spectra except for $\Delta\epsilon_1$ and $\Delta\epsilon_2$ induced by the 0.25-eV excitation are shown by the

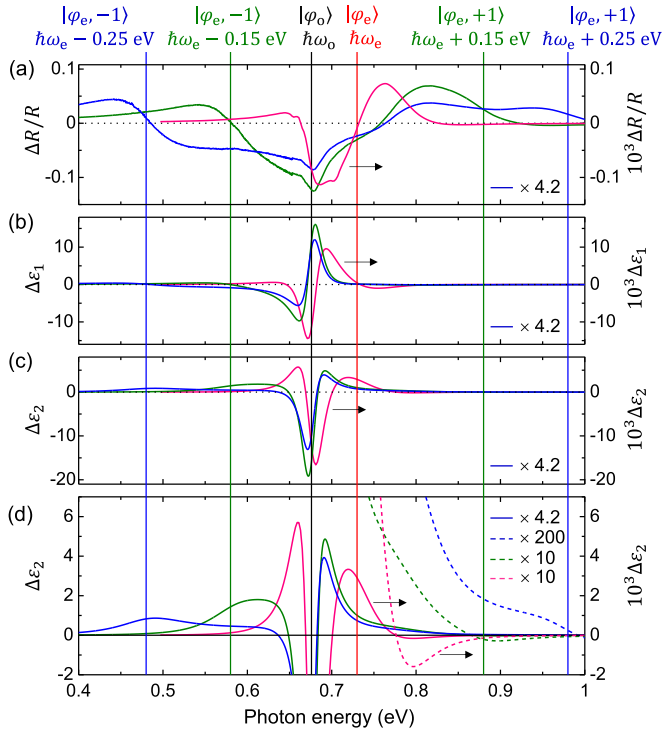


FIG. 6. Simulated spectra based upon the four-level model: (a) $\Delta R/R$; (b) $\Delta\epsilon_1$; and (c), (d) $\Delta\epsilon_2$. Blue lines: the 0.25-eV excitation; green lines: the 0.15-eV excitation; and purple lines: the static electric field.

red lines in Figs. 3(d)–3(l). In the simulated spectra under the static electric field, $\hbar\gamma_0$ is set to 0.018 eV instead of 0.0152 eV as mentioned above. In the three $\Delta\epsilon_2$ spectra in Figs. 6(c) and 6(d), as compared with the original $|\varphi_g\rangle \rightarrow |\varphi_0\rangle$ transition, the $|\varphi_g\rangle \rightarrow |\varphi_0'\rangle$ transition under the static electric field shifts to the lower energy, but the $|\varphi_g\rangle \rightarrow |\varphi_0, 0\rangle$ transition shifts to the higher energy under the 0.25- and 0.15-eV excitations in common. It can also be recognized that under the static electric field, the $|\varphi_g\rangle \rightarrow |\varphi_e'\rangle$ transition becomes optically allowed, gaining the intensity around $\hbar\omega_e$, and that under the 0.25- and 0.15-eV excitations, the $|\varphi_g\rangle \rightarrow |\varphi_e, -1\rangle$ transitions appear around $\hbar\omega_e - 0.25$ eV and $\hbar\omega_e - 0.15$ eV, respectively, as expected, while the spectral weights of the $|\varphi_g\rangle \rightarrow |\varphi_e, +1\rangle$ transitions are located below $\hbar\omega_e + 0.25$ eV and $\hbar\omega_e + 0.15$ eV, respectively, as seen in Fig. 6(d). This is mainly due to the fact that the overlap of the states $|\varphi_0, 0\rangle$ and $|\varphi_e, +1\rangle$ occurs only at the lower energies than $\hbar\omega_e + \hbar\Omega$ as mentioned above. Thus, the energy positions of the electric-field-induced absorptions change systematically when three different electric fields are applied: 0.25-eV excitation, 0.15-eV excitation, and static electric field. These results definitely demonstrate that the observed responses for the 0.25- and 0.15-eV excitations are explained by the Floquet framework.

IV. SUMMARY

In summary, the transient reflectivity spectrum under the MIR electric field was measured in a 1D MIs ET-F₂TCNQ. By analyzing the spectral changes of the complex dielectric constants derived from the transient reflectivity spectrum, the

formation of the excitonic Floquet states was demonstrated. The analysis also revealed that the spectral changes originating from the Floquet sidebands strongly depend on the width of excitonic states. Our approach is effective because Floquet states can be observed using conventional pump-probe spectroscopy. Here, only the first-order sidebands were observed, which correspond to the third-order optical nonlinearity. It is expected that similar experiments using an MIR pulse with a larger electric-field amplitude can detect sidebands of the second order and higher.

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APPENDIX A: ESTIMATIONS OF ELECTRIC FIELDS OF MIR PULSES

The maximum electric field intensity E_{MIR} of an MIR pump pulse can be estimated from its temporal width and its fluence and spot size at the sample surface. The temporal width of the MIR pump pulse τ_p is calculated from the temporal width of the probe pulse τ_r and the temporal characteristic of the reflectivity change due to the coherent response shown in Figs. 3(a) and 3(b).

τ_r is calculated assuming the Fourier limit and using the spectral width (full width at half maximum: FWHM) of the probe pulse. The spectral width (FWHM) of the probe pulse in the frequency domain is approximately 8 THz independent of the probe frequency in common, from which τ_r is determined to be 55 fs. As observed in Figs. 3(a) and 3(b), the temporal width of the reflectivity change due to the coherent response is ~ 135 fs for the 0.25-eV pulse and ~ 450 fs for the 0.15-eV pulse. Here, it is assumed that the temporal profiles of the pump and probe pulses are expressed by Gaussian functions $I_p(t) = \exp(-t^2/\tau_p^2)$ and $I_r(t) = \exp(-t^2/\tau_r^2)$, respectively, and that the time characteristic of the coherent response in the reflectivity change $\Delta R(t)/R$ is also expressed by a Gaussian function as $\Delta R(t)/R \propto \exp(-t^2/\tau_c)$ with τ_c . Because τ_c characterizing the coherent response is determined by the convolution integral of the pump and probe pulses, a relation $\tau_c^2 = \tau_p^2 + \tau_r^2$ stands between τ_p , τ_r , and τ_c . Using this relation, the temporal widths of the 0.25- and 0.15-eV pulses are evaluated to be ~ 123 and ~ 446 fs, respectively. From the spot size of 100 μm (96 μm) and the temporal width

of 123 fs (446 fs), the electric-field amplitude of the MIR pump pulse with 0.25 eV (0.15 eV) used for the measurements

shown in Fig. 3(a) [Fig. 3(b)] is calculated to be 0.66 MV/cm (0.45 MV/cm) from the pulse fluence.

APPENDIX B: THIRD-ORDER NONLINEAR SUSCEPTIBILITY $\chi^{(3)}$ FOR MIR PUMP NIR PROBE SPECTROSCOPY

The third-order nonlinear susceptibility $\chi^{(3)}(-\omega_\sigma; \omega_i, \omega_j, \omega_k)$ is defined by the following formula:

$$P^{(3)}(\omega_\sigma) = 2^{s_\omega-2} p_\omega \varepsilon_0 \chi^{(3)}(-\omega_\sigma; \omega_i, \omega_j, \omega_k) E(\omega_i) E(\omega_j) E(\omega_k). \quad (\text{B1})$$

Here, $P^{(3)}(\omega_\sigma)$ is the third-order nonlinear polarization at frequency ω_σ , $E(\omega_i)$ is the electric field of the incident pulses at frequency ω_i , s_ω is the number of zeros among $(\omega_i, \omega_j, \omega_k)$, and p_ω is the number of permutations of $(\omega_i, \omega_j, \omega_k)$, where $\omega_\sigma = \omega_i + \omega_j + \omega_k$. For the experimental condition of the MIR pump-NIR probe reflection spectroscopy, the change in the complex dielectric constant $\tilde{\varepsilon}(\omega)$, $\Delta\tilde{\varepsilon}(\omega)$, through the third-order nonlinear process is expressed as follows:

$$\Delta\tilde{\varepsilon}(\omega) = \frac{3}{2} \chi^{(3)}(-\omega; \Omega, -\Omega, \omega) E(\Omega) E(-\Omega). \quad (\text{B2})$$

Here, Ω and ω are frequencies of the MIR pump pulse and NIR probe pulse, respectively.

The expression for $\chi^{(3)}(-\omega_\sigma; \omega_i, \omega_j, \omega_k)$ derived from perturbation theory is given by the following formula [41]:

$$\begin{aligned} \chi^{(3)}(-\omega_\sigma; \omega_i, \omega_j, \omega_k) = & \frac{Ne^4}{6\varepsilon_0\hbar^3} \sum_{abc} \langle \varphi_g | x | \varphi_a \rangle \langle \varphi_a | x | \varphi_b \rangle \langle \varphi_b | x | \varphi_c \rangle \langle \varphi_c | x | \varphi_g \rangle \\ & \times \left[\frac{1}{(\omega_a - \omega_\sigma - i\gamma_a)(\omega_b - \omega_j - \omega_k - i\gamma_b)(\omega_c - \omega_k - i\gamma_c)} \right. \\ & + \frac{1}{(\omega_a + \omega_i + i\gamma_a)(\omega_b - \omega_j - \omega_k - i\gamma_b)(\omega_c - \omega_k - i\gamma_c)} \\ & + \frac{1}{(\omega_a + \omega_i + i\gamma_a)(\omega_b + \omega_i + \omega_j + i\gamma_b)(\omega_c - \omega_k - i\gamma_c)} \\ & \left. + \frac{1}{(\omega_a + \omega_i + i\gamma_a)(\omega_b + \omega_i + \omega_j + i\gamma_b)(\omega_c + \omega_\sigma + i\gamma_c)} \right], \quad (\text{B3}) \end{aligned}$$

where N denotes the density of the ET^+ molecules, ε_0 is the permittivity of the vacuum, e is the elementary charge, $\hbar$ is the reduced Plank constant, $|\varphi_g\rangle$ is the wave function of the ground state and $|\varphi_a\rangle$, $|\varphi_b\rangle$, and $|\varphi_c\rangle$ are those of the excited states, $\langle \varphi_l | x | \varphi_m \rangle$ is the transition dipole moment between $|\varphi_l\rangle$ and $|\varphi_m\rangle$, $\hbar\omega_l$ and $\hbar\gamma_l$ are the energy and width of $|\varphi_l\rangle$, respectively, and $\wp$ denotes the permutation of $(\omega_i, \omega_j, \omega_k)$.

Assuming the three-level model with the ground state $|\varphi_g\rangle$, the odd-parity exciton $|\varphi_o\rangle$, and the even-parity exciton $|\varphi_e\rangle$, $\chi^{(3)}(-\omega_\sigma; \omega_i, \omega_j, \omega_k)$ is given as follows [41]:

$$\begin{aligned} \chi^{(3)}(-\omega_\sigma; \omega_i, \omega_j, \omega_k) = & \frac{Ne^4}{6\varepsilon_0\hbar^3} \langle \varphi_g | x | \varphi_o \rangle \langle \varphi_o | x | \varphi_e \rangle \langle \varphi_e | x | \varphi_o \rangle \langle \varphi_o | x | \varphi_g \rangle \times \wp \left[\frac{1}{(\omega_o - \omega_\sigma - i\gamma_o)(\omega_e - \omega_j - \omega_k - i\gamma_e)(\omega_o - \omega_k - i\gamma_o)} \right. \\ & + \frac{1}{(\omega_o + \omega_i + i\gamma_o)(\omega_e - \omega_j - \omega_k - i\gamma_e)(\omega_o - \omega_k - i\gamma_o)} + \frac{1}{(\omega_o + \omega_i + i\gamma_o)(\omega_e + \omega_i + \omega_j + i\gamma_e)(\omega_o - \omega_k - i\gamma_o)} \\ & \left. + \frac{1}{(\omega_o + \omega_i + i\gamma_o)(\omega_e + \omega_i + \omega_j + i\gamma_e)(\omega_o + \omega_\sigma + i\gamma_o)} \right]. \quad (\text{B4}) \end{aligned}$$

Because $\langle \varphi_o | x | \varphi_e \rangle \langle \varphi_e | x | \varphi_o \rangle \gg \langle \varphi_g | x | \varphi_o \rangle \langle \varphi_o | x | \varphi_g \rangle$ in 1D MIs, the terms proportional to $\langle \varphi_g | x | \varphi_o \rangle \langle \varphi_o | x | \varphi_g \rangle \langle \varphi_g | x | \varphi_o \rangle \langle \varphi_o | x | \varphi_g \rangle$ are neglected. For the experimental condition of MIR pump-NIR probe reflection spectroscopy, $\chi^{(3)}(-\omega; \Omega, -\Omega, \omega)$ is given by the following 24 terms [41]:

$$\begin{aligned} \chi^{(3)}(-\omega; \Omega, -\Omega, \omega) = & \frac{Ne^4}{6\varepsilon_0\hbar^3} \langle \varphi_g | x | \varphi_o \rangle \langle \varphi_o | x | \varphi_e \rangle \langle \varphi_e | x | \varphi_o \rangle \langle \varphi_o | x | \varphi_g \rangle \times \left[\frac{1}{(\omega_o - i\gamma_o - \omega)^2 (\omega_e - i\gamma_e + \Omega - \omega)} \right. \\ & + \frac{1}{(\omega_o - i\gamma_o - \omega)(\omega_e - i\gamma_e + \Omega - \omega)(\omega_o - i\gamma_o + \Omega)} \\ & + \frac{1}{(\omega_o - i\gamma_o - \omega)^2 (\omega_e - i\gamma_e - \Omega - \omega)} + \frac{1}{(\omega_o - i\gamma_o - \omega)(\omega_e - i\gamma_e - \Omega - \omega)(\omega_o - i\gamma_o - \Omega)} \end{aligned}$$

$$\begin{aligned}
& + \frac{1}{(\omega_0 - i\gamma_0 - \omega)(\omega_e - i\gamma_e)(\omega_0 - i\gamma_0 + \Omega)} + \frac{1}{(\omega_0 - i\gamma_0 - \omega)(\omega_e - i\gamma_e)(\omega_0 - i\gamma_0 - \Omega)} \\
& + \frac{1}{(\omega_0 + i\gamma_0 + \Omega)(\omega_e - i\gamma_e + \Omega - \omega)(\omega_0 - i\gamma_0 - \omega)} \\
& + \frac{1}{(\omega_0 + i\gamma_0 + \Omega)(\omega_e - i\gamma_e + \Omega - \omega)(\omega_0 - i\gamma_0 + \Omega)} \\
& + \frac{1}{(\omega_0 + i\gamma_0 - \Omega)(\omega_e - i\gamma_e - \Omega - \omega)(\omega_0 - i\gamma_0 - \omega)} \\
& + \frac{1}{(\omega_0 + i\gamma_0 - \Omega)(\omega_e - i\gamma_e - \Omega - \omega)(\omega_0 - i\gamma_0 + \Omega)} \\
& + \frac{1}{(\omega_0 + i\gamma_0 + \omega)(\omega_e - i\gamma_e)(\omega_0 - i\gamma_0 + \Omega)} + \frac{1}{(\omega_0 + i\gamma_0 + \omega)(\omega_e - i\gamma_e)(\omega_0 - i\gamma_0 - \Omega)} \\
& + \frac{1}{(\omega_0 + i\gamma_0 + \Omega)(\omega_e + i\gamma_e)(\omega_0 - i\gamma_0 - \omega)} + \frac{1}{(\omega_0 + i\gamma_0 + \Omega)(\omega_e + i\gamma_e + \Omega + \omega)(\omega_0 - i\gamma_0 + \Omega)} \\
& + \frac{1}{(\omega_0 + i\gamma_0 - \Omega)(\omega_e + i\gamma_e)(\omega_0 - i\gamma_0 - \omega)} + \frac{1}{(\omega_0 + i\gamma_0 - \Omega)(\omega_e + i\gamma_e - \Omega + \omega)(\omega_0 - i\gamma_0 - \Omega)} \\
& + \frac{1}{(\omega_0 + i\gamma_0 + \omega)(\omega_e + i\gamma_e + \Omega + \omega)(\omega_0 - i\gamma_0 + \Omega)} \\
& + \frac{1}{(\omega_0 + i\gamma_0 + \omega)(\omega_e + i\gamma_e - \Omega + \omega)(\omega_0 - i\gamma_0 - \Omega)} \\
& + \frac{1}{(\omega_0 + i\gamma_0 + \Omega)(\omega_e + i\gamma_e)(\omega_0 + i\gamma_0 + \omega)} + \frac{1}{(\omega_0 + i\gamma_0 + \Omega)(\omega_e + i\gamma_e + \Omega + \omega)(\omega_0 + i\gamma_0 + \omega)} \\
& + \frac{1}{(\omega_0 + i\gamma_0 - \Omega)(\omega_e + i\gamma_e)(\omega_0 + i\gamma_0 + \omega)} + \frac{1}{(\omega_0 + i\gamma_0 - \Omega)(\omega_e + i\gamma_e - \Omega + \omega)(\omega_0 + i\gamma_0 + \omega)} \\
& + \frac{1}{(\omega_0 + i\gamma_0 + \omega)^2(\omega_e + i\gamma_e + \Omega + \omega)} + \frac{1}{(\omega_0 + i\gamma_0 + \omega)^2(\omega_e + i\gamma_e - \Omega + \omega)} \Big]. \quad (\text{B5})
\end{aligned}$$

The dominant terms in Eq. (B5) are the first and third ones. However, the $\Delta\tilde{\varepsilon}(\omega)$ spectra experimentally obtained [the green lines in Figs. 3(f)–3(h)] cannot be reproduced by the results of the fitting analysis using this formula (not shown).

Next, we consider the four-level model, in which another odd-parity excited state $|\varphi_{02}\rangle$ is added to the three-level model on the higher energy side than $|\varphi_e\rangle$. In this model, $\chi^{(3)}(-\omega_\sigma; \omega_i, \omega_j, \omega_k)$ is given as follows [41]:

$$\begin{aligned}
& \chi^{(3)}(-\omega_\sigma; \omega_i, \omega_j, \omega_k) \\
& = \frac{Ne^4}{6\varepsilon_0\hbar^3} \langle \varphi_g | x | \varphi_0 \rangle \langle \varphi_0 | x | \varphi_e \rangle \langle \varphi_e | x | \varphi_0 \rangle \langle \varphi_0 | x | \varphi_g \rangle \times \wp \left[\frac{1}{(\omega_0 - \omega_\sigma - i\gamma_0)(\omega_e - \omega_j - \omega_k - i\gamma_e)(\omega_0 - \omega_k - i\gamma_0)} \right. \\
& + \frac{1}{(\omega_0 + \omega_i + i\gamma_0)(\omega_e - \omega_j - \omega_k - i\gamma_e)(\omega_0 - \omega_k - i\gamma_0)} + \frac{1}{(\omega_0 + \omega_i + i\gamma_0)(\omega_e + \omega_i + \omega_j + i\gamma_e)(\omega_0 - \omega_k - i\gamma_0)} \\
& + \left. \frac{1}{(\omega_0 + \omega_i + i\gamma_0)(\omega_e + \omega_i + \omega_j + i\gamma_e)(\omega_0 + \omega_\sigma + i\gamma_0)} \right] + \frac{Ne^4}{6\varepsilon_0\hbar^3} \langle \varphi_g | x | \varphi_0 \rangle \langle \varphi_0 | x | \varphi_e \rangle \langle \varphi_e | x | \varphi_{02} \rangle \langle \varphi_{02} | x | \varphi_g \rangle \\
& \times \wp \left[\frac{1}{(\omega_0 - \omega_\sigma - i\gamma_0)(\omega_e - \omega_j - \omega_k - i\gamma_e)(\omega_{02} - \omega_k - i\gamma_{02})} + \frac{1}{(\omega_0 + \omega_i + i\gamma_0)(\omega_e - \omega_j - \omega_k - i\gamma_e)(\omega_{02} - \omega_k - i\gamma_{02})} \right. \\
& + \frac{1}{(\omega_0 + \omega_i + i\gamma_0)(\omega_e + \omega_i + \omega_j + i\gamma_e)(\omega_{02} - \omega_k - i\gamma_{02})} + \frac{1}{(\omega_0 + \omega_i + i\gamma_0)(\omega_e + \omega_i + \omega_j + i\gamma_e)(\omega_{02} + \omega_\sigma + i\gamma_{02})} \\
& + \frac{1}{(\omega_{02} - \omega_\sigma - i\gamma_{02})(\omega_e - \omega_j - \omega_k - i\gamma_e)(\omega_0 - \omega_k - i\gamma_0)} + \frac{1}{(\omega_{02} + \omega_i + i\gamma_{02})(\omega_e - \omega_j - \omega_k - i\gamma_e)(\omega_0 - \omega_k - i\gamma_0)} \\
& + \left. \frac{1}{(\omega_{02} + \omega_i + i\gamma_{02})(\omega_e + \omega_i + \omega_j + i\gamma_e)(\omega_0 - \omega_k - i\gamma_0)} + \frac{1}{(\omega_{02} + \omega_i + i\gamma_{02})(\omega_e + \omega_i + \omega_j + i\gamma_e)(\omega_0 + \omega_\sigma + i\gamma_0)} \right] \\
& + \frac{Ne^4}{6\varepsilon_0\hbar^3} \langle \varphi_g | x | \varphi_{02} \rangle \langle \varphi_{02} | x | \varphi_e \rangle \langle \varphi_e | x | \varphi_{02} \rangle \langle \varphi_{02} | x | \varphi_g \rangle \times \wp \left[\frac{1}{(\omega_{02} - \omega_\sigma - i\gamma_{02})(\omega_e - \omega_j - \omega_k - i\gamma_e)(\omega_{02} - \omega_k - i\gamma_{02})} \right]
\end{aligned}$$

$$\begin{aligned}
& + \frac{1}{(\omega_{o2} + \omega_i + i\gamma_{o2})(\omega_e - \omega_j - \omega_k - i\gamma_e)(\omega_{o2} - \omega_k - i\gamma_{o2})} + \frac{1}{(\omega_{o2} + \omega_i + i\gamma_{o2})(\omega_e + \omega_i + \omega_j + i\gamma_e)(\omega_{o2} - \omega_k - i\gamma_{o2})} \\
& + \frac{1}{(\omega_{o2} + \omega_i + i\gamma_{o2})(\omega_e + \omega_i + \omega_j + i\gamma_e)(\omega_{o2} + \omega_\sigma + i\gamma_{o2})} \Big]. \quad (\text{B6})
\end{aligned}$$

For the experimental condition of MIR pump-NIR probe reflection spectroscopy, the main terms for $\chi^{(3)}(-\omega; \Omega, -\Omega, \omega)$ are expressed as follows:

$$\begin{aligned}
\chi_{\text{main}}^{(3)}(-\omega; \Omega, -\Omega, \omega) &= \frac{Ne^4}{6\epsilon_0\hbar^3} \langle \varphi_g | x | \varphi_o \rangle \langle \varphi_o | x | \varphi_e \rangle \langle \varphi_e | x | \varphi_o \rangle \langle \varphi_o | x | \varphi_g \rangle \times \left[\frac{1}{(\omega_o - i\gamma_o - \omega)^2(\omega_e - i\gamma_e + \Omega - \omega)} + \frac{1}{(\omega_o - i\gamma_o - \omega)^2(\omega_e - i\gamma_e - \Omega - \omega)} \right] \\
&+ \frac{Ne^4}{3\epsilon_0\hbar^3} \langle \varphi_g | x | \varphi_o \rangle \langle \varphi_o | x | \varphi_e \rangle \langle \varphi_e | x | \varphi_{o2} \rangle \langle \varphi_{o2} | x | \varphi_g \rangle \times \left[\frac{1}{(\omega_o - i\gamma_o - \omega)(\omega_e - i\gamma_e + \Omega - \omega)(\omega_{o2} - i\gamma_{o2} - \omega)} \right. \\
&+ \left. \frac{1}{(\omega_o - i\gamma_o - \omega)(\omega_e - i\gamma_e - \Omega - \omega)(\omega_{o2} - i\gamma_{o2} - \omega)} \right] + \frac{Ne^4}{6\epsilon_0\hbar^3} \langle \varphi_g | x | \varphi_{o2} \rangle \langle \varphi_{o2} | x | \varphi_e \rangle \langle \varphi_e | x | \varphi_{o2} \rangle \langle \varphi_{o2} | x | \varphi_g \rangle \\
&\times \left[\frac{1}{(\omega_{o2} - i\gamma_{o2} - \omega)^2(\omega_e - i\gamma_e + \Omega - \omega)} + \frac{1}{(\omega_{o2} - i\gamma_{o2} - \omega)^2(\omega_e - i\gamma_e - \Omega - \omega)} \right]. \quad (\text{B7})
\end{aligned}$$

The experimental $\Delta\epsilon_1$ and $\Delta\epsilon_2$ spectra can be well reproduced by this formula [the red lines in Figs. 3(f)–3(h)]. The calculation for $\chi^{(3)}(-\omega; \Omega, -\Omega, \omega)$ was actually conducted considering all terms, not just the main ones. Using Eq. (B7), $\Delta\tilde{\epsilon}(\omega)$ was calculated from $\chi^{(3)}(-\omega; \Omega, -\Omega, \omega)$, and we can obtain $\tilde{\epsilon}(\omega) + \Delta\tilde{\epsilon}(\omega)$. From the static reflectivity spectrum $R(\omega)$ and the transient one $R(\omega) + \Delta R(\omega)$, calculated from $\tilde{\epsilon}(\omega) + \Delta\tilde{\epsilon}(\omega)$, the differential reflectivity spectrum $\Delta R/R(\omega)$ can be calculated [the red line in Figs. 3(d) and 3(e)].

APPENDIX C: THIRD-ORDER NONLINEAR SUSCEPTIBILITY $\chi^{(3)}$ FOR ELECTROREFLECTANCE SPECTROSCOPY

The expression of $\chi^{(3)}(-\omega; 0, 0, \omega)$ can be obtained from Eq. (B6). The main terms for $\chi^{(3)}(-\omega; 0, 0, \omega)$ are expressed as follows:

$$\begin{aligned}
\chi_{\text{main}}^{(3)}(-\omega; 0, 0, \omega) &= \frac{Ne^4}{3\epsilon_0\hbar^3} \langle \varphi_g | x | \varphi_o \rangle \langle \varphi_o | x | \varphi_e \rangle \langle \varphi_e | x | \varphi_o \rangle \langle \varphi_o | x | \varphi_g \rangle \times \left[\frac{1}{(\omega_o - i\gamma_o - \omega)^2(\omega_e - i\gamma_e - \omega)} \right] \\
&+ \frac{2Ne^4}{3\epsilon_0\hbar^3} \langle \varphi_g | x | \varphi_o \rangle \langle \varphi_o | x | \varphi_e \rangle \langle \varphi_e | x | \varphi_{o2} \rangle \langle \varphi_{o2} | x | \varphi_g \rangle \times \left[\frac{1}{(\omega_o - i\gamma_o - \omega)(\omega_e - i\gamma_e - \omega)(\omega_{o2} - i\gamma_{o2} - \omega)} \right] \\
&+ \frac{Ne^4}{3\epsilon_0\hbar^3} \langle \varphi_g | x | \varphi_{o2} \rangle \langle \varphi_{o2} | x | \varphi_e \rangle \langle \varphi_e | x | \varphi_{o2} \rangle \langle \varphi_{o2} | x | \varphi_g \rangle \times \left[\frac{1}{(\omega_{o2} - i\gamma_{o2} - \omega)^2(\omega_e - i\gamma_e - \omega)} \right]. \quad (\text{C1})
\end{aligned}$$

The $\Delta\epsilon_1$, $\Delta\epsilon_2$, and $\Delta R/R$ spectra experimentally obtained can be well reproduced [the red lines in Figs. 3(i)–3(l)] using the exact expression of $\chi^{(3)}(-\omega; 0, 0, \omega)$ considering all terms not just the main ones. In this simulation, $\hbar\gamma_1$ was slightly changed from the value (0.0152 eV) in Table I to 0.018 eV, while the other parameters were fixed to the values in Table I used in the analyses of the $\text{Re}\chi^{(3)}(-\omega; \Omega, -\Omega, \omega)$ ($\Delta\epsilon_1$) and $\text{Im}\chi^{(3)}(-\omega; \Omega, -\Omega, \omega)$ ($\Delta\epsilon_2$) spectra.

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